

Glossy liquid composition comprising a block polymer

The present invention relates to a liquid cosmetic composition for making up or caring for the skin, including the scalp, of both the human face and body, and human lips or integuments, for instance the hair, the eyelashes, the eyebrows or the nails, comprising a cosmetically acceptable medium containing a particular block polymer.

There are many cosmetic compositions for which the gloss properties of the deposited film, after application to keratin materials (skin, lips or integuments) are very substantial. Examples that may be mentioned include lipsticks, nail varnishes or certain hair products and certain mascaras.

It is known to cosmetic product formulators that this gloss property is promoted when used is made of oils characterized by a high viscosity and a high refractive index and which also have good pigment or filler dispersing properties when the latter are present in the composition.

In this perspective, the formulator has available several types of raw material, for instance oily polymers such as polybutenes, sold especially under the reference Indopol H100, H300 and H1500 by the company Amoco, which have a very high viscosity but,

however, have the drawback of being both very tacky and of having relatively poor pigment dispersing properties, which limits their use.

The aim of the present invention is to
5 propose a novel route for formulating a cosmetic product, in particular a makeup product, which has good gloss properties.

In particular, the product of the invention makes it possible to obtain continuous deposits on the
10 skin or the lips, which shows good coverage, having a very glossy appearance that meets the desires of consumers, which does not migrate, does not transfer, has good staying power, is not oily, and does not dry out the skin, the hair or the lips to which it is
15 applied, either during the application or over time. It also has good stability properties and thus allows a homogeneous and aesthetic application.

One subject of the invention is a glossy liquid composition for caring for or making up the skin
20 and/or the lips and/or integuments, containing a block polymer, which makes it possible to overcome the drawbacks of the known glossy compositions. The inventors have found, surprisingly, that the use of a sufficient amount of a particular block polymer makes
25 it possible to obtain a glossy composition that also has good staying power.

The composition of the invention may in particular constitute a haircare product or a makeup product for the human body, lips or integuments that has care and/or treating properties. It especially
5 constitutes a lipstick or a lip gloss, an eyeshadow, a tattoo product, a mascara, an eyeliner, a nail varnish, a product for artificially tanning the skin, an optionally tinted care or protecting cream, or a hair-colouring or haircare product.

10 More specifically, the invention relates to a liquid cosmetic composition containing a cosmetically acceptable organic liquid medium, and a non-elastomeric film-forming linear ethylenic block polymer, the said polymer being such that, when it is in sufficient
15 amount in the composition, the mean gloss measured at 20° of a deposit of the said composition, once spread onto a support, is preferably greater than or equal to 30 out of 100.

A subject of the invention is also a liquid
20 cosmetic composition containing a cosmetically acceptable organic liquid medium, and a film-forming linear ethylenic block polymer free of styrene units, the said polymer being such that, when it is in sufficient amount in the composition, the mean gloss
25 measured at 20° of a deposit of the said composition, once spread onto a support, is preferably greater than

or equal to 30 out of 100.

The term "liquid composition" means a composition which, at 25°C and atmospheric pressure, takes the shape of the container into which it is
5 poured.

Preferably, the composition according to the invention is a leave-in composition.

Mean gloss of the composition

The term "mean gloss" means the gloss as may be
10 conventionally measured using a glossmeter by the following method.

A coat of between 50 μm and 150 μm in thickness of the composition is spread using an automatic spreader onto a Leneta brand contrast card of
15 reference Form 1A Penopac. The coat covers at least the white background of the card. The deposit is left to dry for 24 hours at a temperature of 30°C, and the gloss at 20° is then measured on the white background using a Byk Gardner brand glossmeter of reference
20 microTri-Gloss.

This measurement (between 0 and 100) is repeated at least three times, and the mean gloss is the mean of the at least three measurements taken.

The mean gloss of the composition measured at
25 20° is advantageously greater than or equal to 30, better still greater than or equal to 35, even better

still greater than or equal to 40, even better still
greater than or equal to 45, even better still greater
than or equal to 50 out of 100, even better still
greater than or equal to 55, even better still greater
5 than or equal to 60, even better still greater than or
equal to 65, even better still greater than or equal to
70 or, even better still, greater than or equal to 75
out of 100. For certain compositions according to the
invention, such as nail varnishes, the gloss measured
10 at 20° may be greater than or equal to 70, or even 80
out of 100.

Preferably, the mean gloss of the
composition, once spread onto a support, measured at 60°
is greater than or equal to 50, better still greater
15 than or equal to 60, better still greater than or equal
to 65, better still greater than or equal to 70, better
still greater than or equal to 75, better still greater
than or equal to 80, better still greater than or equal
to 85 or, even better still, greater than or equal to
20 90 out of 100.

The mean gloss at 60° is measured as follows.
The gloss may be measured using a glossmeter, in a
conventional manner, by the following method.

A coat of between 50 μm and 150 μm in
25 thickness of the composition is spread using an
automatic spreader onto a Leneta brand contrast card of

reference Form 1A Penopac. The coat covers at least the white background of the card. The deposit is left to dry for 24 hours at a temperature of 30°C, and the gloss at 60° is then measured on the white background
5 using a Byk Gardner brand glossmeter of reference microTri-Gloss.

This measurement (between 0 and 100) is repeated at least three times, and the mean gloss is the mean of the at least three measurements taken.

10 According to one embodiment, the mean gloss of the composition measured at 20° is preferably greater than or equal to 35, preferably 40, 45 or 50 out of 100, and/or the mean gloss of the composition measured at 60° is preferably greater than or equal to
15 65, 70 or 75 out of 100. In this embodiment, the composition advantageously constitutes a liquid lipstick.

According to one embodiment, the mean gloss of the composition measured at 20° is preferably
20 greater than or equal to 60, preferably 65, 70 or 75 out of 100, and/or the mean gloss of the composition measured at 60° is preferably greater than or equal to 80, 85 or 90 out of 100. In this embodiment, the composition advantageously constitutes a nail varnish.

25 The invention also relates to a cosmetic composition comprising an organic liquid medium and at

least one block polymer as described below.

The invention also relates to a process for making up the skin and/or the lips and/or the integuments, which consists in applying the composition
5 as defined above to the skin and/or the lips and/or the integuments.

The composition according to the invention may be applied to the skin of both the face and the scalp, and of the body, mucous membranes, for instance
10 the lips, the inside of the lower eyelids, and integuments, for instance the nails, the eyelashes, the hair, the eyebrows, or even body hairs.

The invention also relates to the use of a block polymer in a sufficient amount in a cosmetic
15 composition to give gloss and/or staying power to a deposit of the said composition.

The invention also relates to the cosmetic use of the composition defined above to improve the gloss of the makeup on the skin and/or the lips and/or
20 integuments.

The composition advantageously contains a small proportion of oils conventionally used to impart gloss, these oils generally being tacky.

The composition according to the invention
25 advantageously contains less than 30%, preferably less than 25%, less than 20% and better still less than 15%

of at least one glossy oil.

The term "oil" means a compound that is immiscible with water in all proportions, and which is liquid at room temperature (25°C) and atmospheric
5 pressure (760 mmHg).

The term "glossy oil" means an oil whose molar mass preferably ranges from 650 to 10 000 g/mol and preferably from 750 to 7500 g/mol.

The oil with a molar mass ranging from 650 to
10 10 000 g/mol may be chosen from:

- lipophilic polymers such as:

- polybutylenes such as Indopol H-100 (molar mass or MM = 965 g/mol), Indopol H-300 (MM = 1340 g/mol) and Indopol H-1500 (MM = 2160 g/mol) sold or
15 manufactured by the company Amoco,
- hydrogenated polyisobutylenes such as Panalane H-300 E sold or manufactured by the company Amoco (MM = 1340 g/mol), Viseal 20000 sold or manufactured by the company Syntel (MM = 6000 g/mol) and
20 Rewopal PIB 1000 sold or manufactured by the company Witco (MM = 1000 g/mol),
- polydecenes and hydrogenated polydecenes such as: Puresyn 10 (MM = 723 g/mol) and Puresyn 150 (MM = 9200 g/mol) sold or manufactured by the company
25 Mobil Chemicals,
- vinylpyrrolidone copolymers such as:

vinylpyrrolidone/1-hexadecene copolymer, Antaron V-216 sold or manufactured by the company ISP (MM = 7300 g/mol),

- esters such as:

- 5 - linear fatty acid esters with a total carbon number ranging from 35 to 70, for instance pentaerythrityl tetrapelargonate (MM = 697.05 g/mol),
- hydroxylated esters such as polyglyceryl-2
10 triisostearate (MM = 965.58 g/mol),
- aromatic esters such as tridecyl trimellitate (MM = 757.19 g/mol),
- esters of branched C₂₄-C₂₈ fatty alcohols or fatty acids such as those described in patent
15 application EP-A-0 955 039, and especially triisoarachidyl citrate (MM = 1033.76 g/mol), pentaerythrityl tetraisononanoate (MM = 697.05 g/mol), glyceryl triisostearate (MM = 891.51 g/mol), glyceryl tris(2-decyl)tetradecanoate (MM =
20 1143.98 g/mol), pentaerythrityl tetraisostearate (MM = 1202.02 g/mol), polyglyceryl-2 tetraisostearate (MM = 1232.04 g/mol) or pentaerythrityl tetrakis(2-decyl)tetradecanoate (MM = 1538.66 g/mol),
- 25 - silicone oils such as phenylsilicones, for instance Belsil PDM 1000 from the company Wacker (MM = 9000

g/mol),

- oils of plant origin, such as sesame oil (820.6

g/mol),

- and mixtures thereof.

5 **Block polymer:**

The composition according to the present invention contains at least one block polymer. The term "block polymer" means a polymer comprising at least two different blocks and preferably at least three

10 different blocks.

According to one embodiment, the block polymer of the composition according to the present invention is an ethylenic polymer. The term "ethylenic polymer" means a polymer obtained by polymerizing

15 monomers comprising an ethylenic unsaturation.

According to one embodiment, the block polymer of the composition according to the present invention is a linear polymer. In contrast, a polymer of non-linear structure is, for example, a polymer of

20 branched, starburst or grafted structure, or the like.

According to one embodiment, the block polymer of the composition according to the present invention is a film-forming polymer. The term "film-forming polymer" means a polymer capable of forming, by

25 itself or in the presence of an auxiliary film-forming agent, a continuous film that adheres to a support and

especially to keratin materials.

According to one embodiment, the block polymer of the composition according to the invention is a non-elastomeric polymer.

5 The term "non-elastomeric polymer" means a polymer which, when it is subjected to a constraint intended to stretch it (for example by 30% relative to its initial length), does not return to a length substantially identical to its initial length when the
10 constraint ceases.

More specifically, the term "non-elastomeric polymer" denotes a polymer with an instantaneous recovery $R_i < 50\%$ and a delayed recovery $R_{2h} < 70\%$ after having been subjected to a 30% elongation. Preferably,
15 R_i is $< 30\%$ and $R_{2h} < 50\%$.

More specifically, the non-elastomeric nature of the polymer is determined according to the following protocol:

A polymer film is prepared by pouring a
20 solution of the polymer in a Teflon-coated mould, followed by drying for 7 days in an environment conditioned at $23 \pm 5^\circ\text{C}$ and $50 \pm 10\%$ relative humidity.

A film about 100 μm thick is thus obtained, from which are cut rectangular specimens (for example
25 using a punch) 15 mm wide and 80 mm long.

This sample is subjected to a tensile stress

using a machine sold under the reference Zwick, under the same temperature and humidity conditions as for the drying.

The specimens are pulled at a speed of
5 50 mm/min and the distance between the jaws is 50 mm, which corresponds to the initial length (l_0) of the specimen.

The instantaneous recovery R_i is determined in the following manner:

- 10 - the specimen is pulled by 30% (ε_{\max}), i.e. about 0.3 times its initial length (l_0)
- the constraint is released by applying a return speed equal to the tensile speed, i.e. 50 mm/min, and the residual elongation of the specimen is measured as a
15 percentage, after returning to zero constraint (ε_i).

The percentage instantaneous recovery (R_i) is given by the following formula:

$$R_i = ((\varepsilon_{\max} - \varepsilon_i) / \varepsilon_{\max}) \times 100$$

20

To determine the delayed recovery, the percentage residual elongation of the specimen (ε_{2h}) is measured, 2 hours after returning to zero constraint.

The percentage delayed recovery (R_{2h}) is given
25 by the following formula:

$$R_{2h} = ((\epsilon_{\max} - \epsilon_{2h}) / \epsilon_{\max}) \times 100$$

Purely as a guide, a polymer according to one embodiment of the invention has an instantaneous
5 recovery R_i of 10% and a delayed recovery R_{2h} of 30%.

According to another embodiment, the block polymer of the composition according to the invention does not comprise any styrene units. The expression "polymer free of styrene units" means a polymer
10 comprising less than 10%, preferably less than 5%, preferentially less than 2% and more preferentially less than 1% by weight i) of styrene units of formula $-\text{CH}(\text{C}_6\text{H}_5)-\text{CH}_2-$ or ii) of substituted styrene units, for instance methylstyrene, chlorostyrene or
15 chloromethylstyrene.

According to one embodiment, the block polymer of the composition according to the invention is derived from aliphatic ethylenic monomers. The term "aliphatic monomer" means a monomer comprising no
20 aromatic groups.

According to one embodiment, the block polymer is an ethylenic polymer derived from aliphatic ethylenic monomers comprising a carbon-carbon double bond and at least one ester group $-\text{COO}-$ or amide group
25 $-\text{CON}-$. The ester group may be linked to one of the two unsaturated carbons via the carbon atom or the oxygen

atom. The amide group may be linked to one of the two unsaturated carbons via the carbon atom or the nitrogen atom.

According to one embodiment, the block
5 polymer comprises at least one first block and at least one second block.

The term "at least one block" means one or more blocks.

It is pointed out that, in the text herein-
10 above and hereinbelow, the terms "first" and "second" blocks do not in any way condition the order of the said blocks in the polymer structure.

According to one embodiment, the block
polymer comprises at least one first block and at least
15 one second block that have different glass transition temperatures (T_g).

In this embodiment, the first and second
blocks may be linked together via an intermediate
segment with a glass transition temperature between the
20 glass transition temperatures of the first and second blocks.

According to one embodiment, the block
polymer comprises at least one first block and at least
one second block linked together via an intermediate
25 segment comprising at least one constituent monomer of the first block and at least one constituent monomer of

the second block.

Preferably, the intermediate block is derived essentially from constituent monomers of the first block and of the second block.

5 The term "essentially" means at least 85%, preferably at least 90%, better still 95% and even better still 100%.

Advantageously, the intermediate segment comprising at least one constituent monomer of the
10 first block and at least one constituent monomer of the second block of the polymer is a random polymer.

According to one embodiment, the block polymer comprises at least one first block and at least one second block that are incompatible in the organic
15 liquid medium of the composition of the invention.

The term "mutually incompatible blocks" means that the mixture formed from the polymer corresponding to the first block and from the polymer corresponding to the second block is not miscible in the liquid that
20 is in major amount by weight contained in the organic liquid medium of the composition, at room temperature (25°C) and atmospheric pressure (10^5 Pa), for a content of the polymer mixture of greater than or equal to 5% by weight, relative to the total weight of the mixture
25 (polymers and major organic liquid), it being understood that:

- i) the said polymers are present in the mixture in a content such that the respective weight ratio ranges from 10/90 to 90/10, and
- ii) each of the polymers corresponding to the first and second blocks has an average (weight-average or number-average) molecular mass equal to that of the block polymer $\pm 15\%$.

When the organic liquid medium comprises a mixture of organic liquids, in the case of two or more liquids present in identical mass proportions, the said polymer mixture is immiscible in at least one of them.

When the organic liquid medium comprises only one organic liquid, this liquid obviously constitutes the liquid that is in major amount by weight.

The term "organic liquid medium" means a medium containing at least one organic liquid, i.e. at least one organic compound that is liquid at room temperature (25°C) and atmospheric pressure (10⁵ Pa). According to one embodiment, the major liquid of the organic liquid medium is a volatile or non-volatile oil (fatty substance). Preferably, the organic liquid is cosmetically acceptable (acceptable tolerance, toxicology and feel). The organic liquid medium is cosmetically acceptable, in the sense that it is compatible with keratin materials, for instance the oils or organic solvents commonly used in cosmetic

compositions.

According to one embodiment, the major liquid of the organic liquid medium is the polymerization solvent or one of the polymerization solvents of the
5 block polymer, as are described below.

The term "polymerization solvent" means a solvent or a mixture of solvents. The polymerization solvent may be chosen especially from ethyl acetate, butyl acetate, alcohols such as isopropanol and
10 ethanol, aliphatic alkanes such as isododecane, and mixtures thereof. Preferably, the polymerization solvent is a mixture of butyl acetate and isopropanol, or isododecane.

In general, the block polymer may be
15 incorporated into the composition to a high solids content, typically greater than 10%, greater than 20%, more preferably greater than 30% and more preferentially greater than 45% by weight relative to the total weight of the composition, while at the same
20 time being easy to formulate.

Preferably, the block polymer comprises no silicon atoms in its skeleton. The term "skeleton" means the main chain of the polymer, as opposed to the pendent side chains.

25 Preferably, the polymer according to the invention is not water-soluble, i.e. the polymer is not

soluble in water or in a mixture of water and linear or branched lower monoalcohols containing from 2 to 5 carbon atoms, for instance ethanol, isopropanol or n-propanol, without pH modification, at an active material content of at least 1% by weight, at room temperature (25°C).

According to one embodiment, the block polymer has a polydispersity index I of greater than 2.

Advantageously, the block polymer used in the compositions according to the invention has a polydispersity index I of greater than 2, for example ranging from 2 to 9, preferably greater than or equal to 2.5, for example ranging from 2.5 to 8 and better still greater than or equal to 2.8, and especially ranging from 2.8 to 6.

The polydispersity index I of the polymer is equal to the ratio of the weight-average mass M_w to the number-average mass M_n .

The weight-average molar mass (M_w) and number-average molar mass (M_n) are determined by gel permeation liquid chromatography (THF solvent, calibration curve established with linear polystyrene standards, refractometric detector).

The weight-average mass (M_w) of the block polymer is preferably less than or equal to 300 000; it ranges, for example, from 35 000 to 200 000 and better

still from 45 000 to 150 000.

The number-average mass (M_n) of the block polymer is preferably less than or equal to 70 000; it ranges, for example, from 10 000 to 60 000 and better
5 still from 12 000 to 50 000.

Each block of the block polymer is derived from one type of monomer or from several different types of monomer.

This means that each block may consist of a
10 homopolymer or a copolymer; this copolymer constituting the block may in turn be random or alternating.

The glass transition temperatures indicated for the first and second blocks may be theoretical T_g values determined from the theoretical T_g values of the
15 constituent monomers of each of the blocks, which may be found in a reference manual such as the Polymer Handbook, 3rd Edition, 1989, John Wiley, according to the following relationship, known as Fox's law:

20
$$1/T_g = \sum_i (\omega_i/T_{g_i}),$$

ω_i being the mass fraction of the monomer i in the block under consideration and T_{g_i} being the glass transition temperature of the homopolymer of the monomer i .

25 Unless otherwise indicated, the T_g values

indicated for the first and second blocks in the present patent application are theoretical Tg values.

The difference between the glass transition temperatures of the first and second blocks is
5 generally greater than 10°C, preferably greater than 20°C and better still greater than 30°C.

In particular, the block polymer comprises at least one first block and at least one second block such that the first block may be chosen from:

- 10 - a) a block with a Tg of greater than or equal to 40°C,
 - b) a block with a Tg of less than or equal to 20°C,
 - c) a block with a Tg of between 20 and 40°C,
- 15 and the second block can be chosen from a category a), b) or c) different from the first block.

In the present invention, the expression:
"between ... and ..." is intended to denote a range of values for which the limits mentioned are excluded, and
20 "from ... to ..." and "ranging from ... to ..." are intended to denote a range of values for which the limits are included.

a) Block with a Tg of greater than or equal to 40°C

The block with a Tg of greater than or equal
25 to 40°C has, for example, a Tg ranging from 40 to 150°C, preferably greater than or equal to 50°C, for

example ranging from 50°C to 120°C and better still greater than or equal to 60°C, for example ranging from 60°C to 120°C.

The block with a Tg of greater than or equal to 40°C may be a homopolymer or a copolymer.

The block with a Tg of greater than or equal to 40°C may be totally or partially derived from one or more monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature of greater than or equal to 40°C.

In the case where this block is a homopolymer, it is derived from monomers which are such that the homopolymers prepared from these monomers have glass transition temperatures of greater than or equal to 40°C. This first block may be a homopolymer consisting of only one type of monomer (for which the Tg of the corresponding homopolymer is greater than or equal to 40°C).

In the case where the first block is a copolymer, it may be totally or partially derived from one or more monomers, the nature and concentration of which are chosen such that the Tg of the resulting copolymer is greater than or equal to 40°C. The copolymer may comprise, for example:

- monomers which are such that the homopolymers prepared from these monomers have Tg values of greater

than or equal to 40°C, for example a Tg ranging from 40 to 150°C, preferably greater than or equal to 50°C, for example ranging from 50°C to 120°C and better still greater than or equal to 60°C, for example ranging from
 5 60°C to 120°C, and

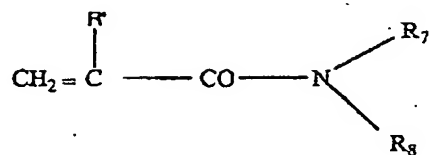
- monomers which are such that the homopolymers prepared from these monomers have Tg values of less than 40°C, chosen from monomers with a Tg of between 20 and 40°C and/or monomers with a Tg of less than or
 10 equal to 20°C, for example a Tg ranging from -100 to 20°C, preferably less than 15°C, especially ranging from -80°C to 15°C and better still less than 10°C, for example ranging from -50°C to 0°C, as described later.

The monomers whose homopolymers have a glass
 15 transition temperature of greater than or equal to 40°C are chosen, preferably, from the following monomers, also known as the main monomers:

- methacrylates of formula $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{COOR}_1$
 in which R_1 represents a linear or branched
 20 unsubstituted alkyl group containing from 1 to 4 carbon atoms, such as a methyl, ethyl, propyl or isobutyl group or R_1 represents a C_4 to C_{12} cycloalkyl group,

- acrylates of formula $\text{CH}_2 = \text{CH} - \text{COOR}_2$
 25 in which R_2 represents a C_4 to C_{12} cycloalkyl group such as isobornyl acrylate or a tert-butyl group,

- (meth)acrylamides of formula:



in which R₇ and R₈, which may be identical or different, each represent a hydrogen atom or a linear or branched C₁ to C₁₂ alkyl group such as an n-butyl, t-butyl, isopropyl, isohexyl, isooctyl or isononyl group; or R₇ represents H and R₈ represents a 1,1-dimethyl-3-oxobutyl group, and R' denotes H or methyl. Examples of monomers that may be mentioned include N-butylacrylamide, N-t-butylacrylamide, N-isopropylacrylamide, N,N-dimethylacrylamide and N,N-dibutylacrylamide, and mixtures thereof.

Main monomers that are particularly preferred are methyl methacrylate, isobutyl (meth)acrylate and isobornyl (meth)acrylate, and mixtures thereof.

b) Block with a Tg of less than or equal to 20°C

The block with a Tg of less than or equal to 20°C has, for example, a Tg ranging from -100 to 20°C, preferably less than or equal to 15°C, especially ranging from -80°C to 15°C and better still less than or equal to 10°C, for example ranging from -50°C to 0°C.

The block with a Tg of less than or equal to

20°C may be a homopolymer or a copolymer.

The block with a Tg of less than or equal to 20°C may be totally or partially derived from one or more monomers, which are such that the homopolymer
5 prepared from these monomers has a glass transition temperature of less than or equal to 20°C.

In the case where this block is a homopolymer, it is derived from monomers which are such that the homopolymers prepared from these monomers have
10 glass transition temperatures of less than or equal to 20°C. This second block may be a homopolymer consisting of only one type of monomer (for which the Tg of the corresponding homopolymer is less than or equal to 20°C).

15 In the case where the block with a Tg of less than or equal to 20°C is a copolymer, it may be totally or partially derived from one or more monomers, the nature and concentration of which are chosen such that the Tg of the resulting copolymer is less than or equal
20 to 20°C.

It may comprise, for example

- one or more monomers whose corresponding homopolymer has a Tg of less than or equal to 20°C, for example a Tg ranging from -100°C to 20°C, preferably less than
25 15°C, especially ranging from -80°C to 15°C and better still less than 10°C, for example ranging from -50°C to

0°C, and

- one or more monomers whose corresponding homopolymer has a Tg of greater than 20°C, such as monomers with a Tg of greater than or equal to 40°C, for example a Tg ranging from 40 to 150°C, preferably greater than or equal to 50°C, for example ranging from 50°C to 120°C and better still greater than or equal to 60°C, for example ranging from 60°C to 120°C and/or monomers with a Tg of between 20 and 40°C, as described above.

10 Preferably, the block with a Tg of less than or equal to 20°C is a homopolymer.

The monomers whose homopolymer has a Tg of less than or equal to 20°C are preferably chosen from the following monomers, or main monomer:

- 15 - acrylates of formula $\text{CH}_2 = \text{CHCOOR}_3$,
 R_3 representing a linear or branched C_1 to C_{12} unsubstituted alkyl group, with the exception of the tert-butyl group, in which one or more hetero atoms chosen from O, N and S is (are) optionally
 20 intercalated,
- methacrylates of formula $\text{CH}_2 = \text{C}(\text{CH}_3)\text{-COOR}_4$,
 R_4 representing a linear or branched C_6 to C_{12} unsubstituted alkyl group, in which one or more hetero atoms chosen from O, N and S is (are)
 25 optionally intercalated;
- vinyl esters of formula $\text{R}_5\text{-CO-O-CH} = \text{CH}_2$

in which R_5 represents a linear or branched C_4 to C_{12} alkyl group;

- C_4 to C_{12} alkyl vinyl ethers,
- $N-(C_4 \text{ to } C_{12})$ alkyl acrylamides, such as
- 5 N-octylacrylamide,
- and mixtures thereof.

The main monomers that are particularly preferred for the block with a T_g of less than or equal to 20°C are alkyl acrylates whose alkyl chain contains

10 from 1 to 10 carbon atoms, with the exception of the tert-butyl group, such as methyl acrylate, isobutyl acrylate and 2-ethylhexyl acrylate, and mixtures thereof.

c) Block with a T_g of between 20 and 40°C

15 The block with a T_g of between 20 and 40°C may be a homopolymer or a copolymer.

The block with a T_g of between 20 and 40°C may be totally or partially derived from one or more monomers, which are such that the homopolymer prepared

20 from these monomers has a glass transition temperature of between 20 and 40°C .

The block with a T_g of between 20 and 40°C may be totally or partially derived from monomers, which are such that the corresponding homopolymer has a

25 T_g of greater than or equal to 40°C and from monomers which are such that the corresponding homopolymer has a

Tg of less than or equal to 20°C.

In the case where this block is a homopolymer, it is derived from monomers (or main monomer) which are such that the homopolymers prepared from these monomers have glass transition temperatures of between 20 and 40°C. This first block may be a homopolymer, consisting of only one type of monomer (for which the Tg of the corresponding homopolymer ranges from 20°C to 40°C).

The monomers whose homopolymer has a glass transition temperature of between 20 and 40°C are preferably chosen from n-butyl methacrylate, cyclodecyl acrylate, neopentyl acrylate and isodecylacrylamide, and mixtures thereof.

In the case where the block with a Tg of between 20 and 40°C is a copolymer, it is totally or partially derived from one or more monomers (or main monomer) whose nature and concentration are chosen such that the Tg of the resulting copolymer is between 20 and 40°C.

Advantageously, the block with a Tg of between 20 and 40°C is a copolymer totally or partially derived from:

- main monomers whose corresponding homopolymer has a Tg of greater than or equal to 40°C, for example a Tg ranging from 40°C to 150°C, preferably greater than or

equal to 50°C, for example ranging from 50 to 120°C and better still greater than or equal to 60°C, for example ranging from 60°C to 120°C, as described above, and/or - main monomers whose corresponding homopolymer has a
5 Tg of less than or equal to 20°C, for example a Tg ranging from -100 to 20°C, preferably less than or equal to 15°C, especially ranging from -80°C to 15°C and better still less than or equal to 10°C, for example ranging from -50°C to 0°C, as described above,
10 the said monomers being chosen such that the Tg of the copolymer forming the first block is between 20 and 40°C.

Such main monomers are chosen, for example, from methyl methacrylate, isobornyl acrylate and
15 methacrylate, butyl acrylate and 2-ethylhexyl acrylate, and mixtures thereof.

Preferably, the proportion of the second block with a Tg of less than or equal to 20°C ranges from 10% to 85%, better still from 20% to 70% and even
20 better still from 20% to 50% by weight of the polymer.

Preferably, each of the first and second blocks comprises at least one monomer chosen from acrylic acid, acrylic acid esters, methacrylic acid and methacrylic acid esters, and mixtures thereof.

25 Advantageously, each of the first and second blocks is totally derived from at least one monomer

chosen from acrylic acid, acrylic acid esters, methacrylic acid and methacrylic acid esters, and mixtures thereof.

However, each of the blocks may contain in
5 small proportion at least one constituent monomer of the other block.

Thus, the first block may contain at least one constituent monomer of the second block, and vice versa.

10 Each of the first and/or second blocks may comprise, in addition to the monomers indicated above, one or more other monomers known as additional monomers, which are different from the main monomers mentioned above.

15 The nature and amount of this or these additional monomer(s) are chosen such that the block in which they are present has the desired glass transition temperature.

This additional monomer is chosen, for
20 example, from:

a) hydrophilic monomers such as:

- ethylenically unsaturated monomers comprising at least one carboxylic or sulfonic acid function, for instance:

25 acrylic acid, methacrylic acid, crotonic acid, maleic anhydride, itaconic acid, fumaric acid,

maleic acid, acrylamidopropanesulfonic acid, vinylbenzoic acid, vinylphosphoric acid, and salts thereof,

5 - ethylenically unsaturated monomers comprising at least one tertiary amine function, for instance 2-vinylpyridine, 4-vinylpyridine, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate and dimethylaminopropylmethacrylamide, and salts thereof,

10 - methacrylates of formula $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{COOR}_6$ in which R_6 represents a linear or branched alkyl group containing from 1 to 4 carbon atoms, such as a methyl, ethyl, propyl or isobutyl group, the said alkyl group being substituted with one or
15 more substituents chosen from hydroxyl groups (for instance 2-hydroxypropyl methacrylate and 2-hydroxyethyl methacrylate) and halogen atoms (Cl, Br, I or F), such as trifluoroethyl methacrylate,

20 - methacrylates of formula $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{COOR}_9$, R_9 representing a linear or branched C_6 to C_{12} alkyl group in which one or more hetero atoms chosen from O, N and S is (are) optionally intercalated, the said alkyl group being substituted with one or
25 more substituents chosen from hydroxyl groups and halogen atoms (Cl, Br, I or F);

- acrylates of formula $\text{CH}_2 = \text{CHCOOR}_{10}$,

R_{10} representing a linear or branched C_1 to C_{12}

alkyl group substituted with one or more

substituents chosen from hydroxyl groups and

5 halogen atoms (Cl, Br, I or F), such as

2-hydroxypropyl acrylate and 2-hydroxyethyl

acrylate, or R_{10} represents a C_1 to C_{12} alkyl-O-POE

(polyoxyethylene) with repetition of the

oxyethylene unit 5 to 30 times, for example

10 methoxy-POE, or

R_{10} represents a polyoxyethylenated group

comprising from 5 to 30 ethylene oxide units

b) ethylenically unsaturated monomers comprising

one or more silicon atoms, such as methacryloxy-

15 propyltrimethoxysilane and methacryloxypropyl-

tris(trimethylsiloxy)silane,

- and mixtures thereof.

Additional monomers that are particularly preferred are acrylic acid, methacrylic acid and
20 trifluoroethyl methacrylate, and mixtures thereof.

According to one embodiment, each of the first and second blocks of the block polymer comprises at least one monomer chosen from (meth)acrylic acid esters and optionally at least one additional monomer
25 such as (meth)acrylic acid, and mixtures thereof.

According to another embodiment, each of the

first and second blocks of the block polymer is totally derived from at least one monomer chosen from (meth)acrylic acid esters and optionally at least one additional monomer such as (meth)acrylic acid, and
5 mixtures thereof.

According to one preferred embodiment, the block polymer is a non-silicone polymer, i.e. a polymer free of silicon atoms.

This or these additional monomer(s) generally
10 represent(s) an amount of less than or equal to 30% by weight, for example from 1% to 30% by weight, preferably from 5% to 20% by weight and more preferably from 7% to 15% by weight, relative to the total weight of the first and/or second blocks.

15 The block polymer may be obtained by free-radical solution polymerization according to the following preparation process:

- a portion of the polymerization solvent is introduced into a suitable reactor and heated
20 until the adequate temperature for the polymerization is reached (typically between 60 and 120°C),
- once this temperature is reached, the constituent monomers of the first block are
25 introduced in the presence of some of the polymerization initiator,

- after a time T corresponding to a maximum degree of conversion of 90%, the constituent monomers of the second block and the rest of the initiator are introduced,
- 5 - the mixture is left to react for a time T' (ranging from 3 to 6 hours), after which the mixture is cooled to room temperature,
- the polymer dissolved in the polymerization solvent is obtained.

10 First embodiment

According to a first embodiment, the block polymer comprises a first block with a Tg of greater than or equal to 40°C, as described above in a) and a second block with a Tg of less than or equal to 20°C,
15 as described above in b).

Preferably, the first block with a Tg of greater than or equal to 40°C is a copolymer derived from monomers which are such that the homopolymer prepared from these monomers has a glass transition
20 temperature of greater than or equal to 40°C, such as the monomers described above.

Advantageously, the second block with a Tg of less than or equal to 20°C is a homopolymer derived from monomers which are such that the homopolymer
25 prepared from these monomers has a glass transition temperature of less than or equal to 20°C, such as the

monomers described above.

Preferably, the proportion of the block with a Tg of greater than or equal to 40°C ranges from 20% to 90%, better still from 30% to 80% and even better still from 50% to 70% by weight of the polymer.

Preferably, the proportion of the block with a Tg of less than or equal to 20°C ranges from 5% to 75%, preferably from 15% to 50% and better still from 25% to 45% by weight of the polymer.

Thus, according to a first variant, the polymer according to the invention may comprise:

- a first block with a Tg of greater than or equal to 40°C, for example having a Tg ranging from 70 to 110°C, which is a methyl methacrylate/acrylic acid copolymer,
- a second block with a Tg of less than or equal to 20°C, for example ranging from 0 to 20°C, which is a methyl acrylate homopolymer, and
- an intermediate block which is a methyl methacrylate/acrylic acid/methyl acrylate copolymer.

According to a second variant, the polymer according to the invention may comprise:

- a first block with a Tg of greater than or equal to 40°C, for example ranging from 70 to 100°C, which is a methyl methacrylate/acrylic acid/trifluoroethyl methacrylate copolymer,
- a second block with a Tg of less than or equal to

20°C, for example ranging from 0 to 20°C, which is a methyl acrylate homopolymer, and

- an intermediate block which is a methyl methacrylate/acrylic acid/methyl

5 acrylate/trifluoroethyl methacrylate random copolymer.

According to a third variant, the polymer according to the invention may comprise:

- a first block with a Tg of greater than or equal to 40°C, for example ranging from 85 to 115°C, which is an

10 isobornyl acrylate/isobutyl methacrylate copolymer,

- a second block with a Tg of less than or equal to 20°C, for example ranging from -85 to -55°C, which is a 2-ethylhexyl acrylate homopolymer, and

- an intermediate block, which is an isobornyl
15 acrylate/isobutyl methacrylate/2-ethylhexyl acrylate random copolymer.

According to a fourth variant, the polymer according to the invention may comprise:

- a first block with a Tg of greater than or equal to

20 40°C, for example ranging from 85 to 115°C, which is an isobornyl acrylate/methyl methacrylate copolymer,

- a second block with a Tg of less than or equal to 20°C, for example ranging from -85 to -55°C, which is a 2-ethylhexyl acrylate homopolymer, and

25 - an intermediate block which is an isobornyl acrylate/methyl methacrylate/2-ethylhexyl acrylate

random copolymer.

According to a fifth variant, the polymer according to the invention may comprise:

- a first block with a Tg of greater than or equal to 40°C, for example ranging from 95 to 125°C, which is an isobornyl acrylate/isobornyl methacrylate copolymer,
- a second block with a Tg of less than or equal to 20°C, for example ranging from -85 to -55°C, which is a 2-ethylhexyl acrylate homopolymer, and
- an intermediate block which is an isobornyl acrylate/isobornyl methacrylate/2-ethylhexyl acrylate random copolymer.

According to a sixth variant, the polymer according to the invention may comprise:

- a first block with a Tg of greater than or equal to 40°C, for example ranging from 85 to 115°C, which is an isobornyl methacrylate/isobutyl methacrylate copolymer,
- a second block with a Tg of less than or equal to 20°C, for example ranging from -35 to -5°C, which is an isobutyl acrylate homopolymer, and
- an intermediate block which is an isobornyl methacrylate/isobutyl methacrylate/isobutyl acrylate random copolymer.

According to a seventh variant, the polymer according to the invention may comprise:

- a first block with a Tg of greater than or equal to

40°C, for example ranging from 95 to 125°C, which is an isobornyl acrylate/isobornyl methacrylate copolymer,
- a second block with a Tg of less than or equal to 20°C, for example ranging from -35 to -5°C, which is an
5 isobutyl acrylate homopolymer, and
- an intermediate block which is an isobornyl acrylate/isobornyl methacrylate/isobutyl acrylate random copolymer.

According to an eighth variant, the polymer
10 according to the invention may comprise:
- a first block with a Tg of greater than or equal to 40°C, for example ranging from 60 to 90°C, which is an isobornyl acrylate/isobutyl methacrylate copolymer,
- a second block with a Tg of less than or equal to
15 20°C, for example ranging from -35 to -5°C, which is an isobutyl acrylate homopolymer, and
- an intermediate block which is an isobornyl acrylate/isobutyl methacrylate/isobutyl acrylate random copolymer.

20 The examples that follow illustrate, in a non-limiting manner, polymers corresponding to this first embodiment.

The amounts are expressed in grams.

Example 1: Preparation of a poly(methyl methacrylate/
25 acrylic acid/methyl acrylate) polymer

100 g of butyl acetate are introduced into a

1 litre reactor and the temperature is then raised so as to pass from room temperature (25°C) to 90°C in 1 hour.

180 g of methyl methacrylate, 30 g of acrylic acid,
5 40 g of butyl acetate, 70 g of isopropanol and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox[®] 141 from Akzo Nobel) are then added at 90°C and over 1 hour.

The mixture is maintained at 90°C for 1 hour.

10 90 g of methyl acrylate, 70 g of butyl acetate, 20 g of isopropanol and 1.2 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane are then introduced into the above mixture, still at 90°C and over 1 hour.

15 The mixture is maintained at 90°C for 3 hours and then diluted with 105 g of butyl acetate and 45 g of isopropanol, and the mixture is then cooled.

A solution containing 40% polymer active material in a butyl acetate/isopropanol mixture is
20 obtained.

A polymer comprising a poly(methyl methacrylate/acrylic acid) first block with a Tg of 100°C, a polymethyl acrylate second block with a Tg of 10°C and an intermediate block which is a methyl
25 methacrylate/acrylic acid/polymethyl acrylate random polymer is obtained.

This polymer has a weight-average mass of 52 000 and a number-average mass of 18 000, i.e. a polydispersity index I of 2.89.

**Example 2: Preparation of a poly(isobornyl acrylate/
5 isobutyl methacrylate/2-ethylhexyl acrylate) polymer**

100 g of isododecane are introduced into a 1 litre reactor and the temperature is then increased so as to pass from room temperature (25°C) to 90°C over 1 hour.

10 120 g of isobornyl acrylate, 90 g of isobutyl methacrylate, 110 g of isododecane and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox[®] 141 from Akzo Nobel) are then added, at 90°C and over 1 hour.

15 The mixture is maintained at 90°C for 1 hour 30 minutes.

90 g of 2-ethylhexyl acrylate, 90 g of isododecane and 1.2 g of 2,5-bis(2-ethylhexanoyl-peroxy)-2,5-dimethylhexane are then introduced into the 20 above mixture, still at 90°C and over 30 minutes.

The mixture is maintained at 90°C for 3 hours and is then cooled.

A solution containing 50% polymer active material in isododecane is obtained.

25 A polymer comprising a poly(isobornyl acrylate/isobutyl methacrylate) first block with a Tg

of 80°C, a poly-2-ethylhexyl acrylate second block with a T_g of -70°C and an intermediate block which is an isobornyl acrylate/isobutyl methacrylate/2-ethylhexyl acrylate random polymer is obtained.

5 This polymer has a weight-average mass of 77 000 and a number-average mass of 19 000, i.e. a polydispersity index I of 4.05.

**Example 3: Preparation of a poly(isobornyl acrylate/
isobornyl methacrylate/2-ethylhexyl acrylate) polymer**

10 100 g of isododecane are introduced into a 1 litre reactor and the temperature is then increased so as to pass from room temperature (25°C) to 90°C over 1 hour.

105 g of isobornyl acrylate, 105 g of isobornyl
15 methacrylate, 110 g of isododecane and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox[®] 141 from Akzo Nobel) are then added, at 90°C and over 1 hour.

The mixture is maintained at 90°C for 1 hour
20 30 minutes.

90 g of 2-ethylhexyl acrylate, 90 g of isododecane and 1.2 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane are then introduced into the above mixture, still at 90°C and over 30 minutes.

25 The mixture is maintained at 90°C for 3 hours and is then cooled.

A solution containing 50% polymer active material in isododecane is obtained.

A polymer comprising a poly(isobornyl acrylate/isobornyl methacrylate) first block with a Tg of 110°C, a poly-2-ethylhexyl acrylate second block with a Tg of -70°C and an intermediate block which is an isobornyl acrylate/isobornyl methacrylate/2-ethylhexyl acrylate random polymer is obtained.

This polymer has a weight-average mass of 103 900 and a number-average mass of 21 300, i.e. a polydispersity index I of 4.89.

Example 4: Preparation of a poly(isobornyl acrylate/isobutyl methacrylate/isobutyl acrylate)

polymer

100 g of isododecane are introduced into a 1 litre reactor and the temperature is then increased so as to pass from room temperature (25°C) to 90°C over 1 hour.

120 g of isobornyl acrylate, 90 g of isobutyl methacrylate, 110 g of isododecane and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox® 141 from Akzo Nobel) are then added, at 90°C and over 1 hour.

The mixture is maintained at 90°C for 1 hour 30 minutes.

90 g of isobutyl acrylate, 90 g of isododecane and 1.2 g of 2,5-bis(2-ethylhexanoyl-peroxy)-2,5-dimethylhexane are then introduced into the above mixture, still at 90°C and over 30 minutes.

5 The mixture is maintained at 90°C for 3 hours and is then cooled.

A solution containing 50% polymer active material in isododecane is obtained.

A polymer comprising a poly(isobornyl
10 acrylate/isobutyl methacrylate) first block with a Tg of 75°C, a polyisobutyl acrylate second block with a Tg of -20°C and an intermediate block which is an isobornyl acrylate/isobutyl methacrylate/isobutyl acrylate random polymer is obtained.

15 Example 5: Preparation of a poly(methyl methacrylate/
methyl acrylate/acrylic acid) polymer

100 g of butyl acetate are introduced into a 1 litre reactor and the temperature is then increased so as to pass from room temperature (25°C) to 90°C over
20 1 hour.

50.4 g of methyl methacrylate, 21 g of acrylic acid, 138.6 g of methyl acrylate, 40 g of butyl acetate, 70 g of isopropanol and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox[®] 141
25 from Akzo Nobel) are then added, at 90°C and over 1 hour.

The mixture is maintained at 90°C for 1 hour.

90 g of methyl methacrylate, 70 g of butyl acetate, 20 g of isopropanol and 1.2 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane are then
5 introduced into the above mixture, still at 90°C and over 1 hour.

The mixture is maintained at 90°C for 3 hours and is then diluted with 105 g of butyl acetate and 45 g of isopropanol and cooled.

10 A solution containing 40% polymer active material in butyl acetate/isopropanol is obtained.

The polymer obtained comprises a poly(methyl acrylate/methyl methacrylate/acrylic acid) first block with a Tg of 35°C, a poly(methyl methacrylate) second
15 block with a Tg of 100°C and an intermediate block which is a methyl methacrylate/acrylic acid/polymethyl acrylate random polymer.

Example 6: Preparation of a poly(isobornyl acrylate/isobornyl methacrylate/isobutyl acrylate) polymer

20 100 g of isododecane are introduced into a 1 litre reactor and the temperature is then increased so as to pass from room temperature (25°C) to 90°C over 1 hour.

105 g of isobornyl acrylate, 105 g of isobornyl
25 methacrylate, 110 g of isododecane and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane

(Trigonox[®] 141 from Akzo Nobel) are then added, at 90°C and over 1 hour.

The mixture is maintained at 90°C for 1 hour 30 minutes.

5 90 g of isobutyl acrylate, 90 g of isododecane and 1.2 g of 2,5-bis(2-ethylhexanoyl-peroxy)-2,5-dimethylhexane are then introduced into the above mixture, still at 90°C and over 30 minutes.

The mixture is maintained at 90°C for 3 hours
10 and is then cooled.

A solution containing 50% polymer active material in isododecane is obtained.

A polymer comprising a poly(isobornyl acrylate/isobornyl methacrylate) first block with a Tg
15 of 110°C, a polyisobutyl acrylate second block with a Tg of -20°C and an intermediate block which is an isobornyl acrylate/isobornyl methacrylate/isobutyl acrylate random polymer is obtained.

This polymer has a weight-average mass of
20 151 000 and a number-average mass of 41 200, i.e. a polydispersity index I of 3.66.

Example 7: Preparation of a poly(isobornyl methacrylate/isobutyl methacrylate/isobutyl acrylate) polymer

25 100 g of isododecane are introduced into a 1 litre reactor and the temperature is then increased

so as to pass from room temperature (25°C) to 90°C over 1 hour.

120 g of isobornyl methacrylate, 90 g of isobutyl methacrylate, 110 g of isododecane and 1.8 g of
5 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox® 141 from Akzo Nobel) are then added, at 90°C and over 1 hour.

The mixture is maintained at 90°C for 1 hour 30 minutes.

10 90 g of isobutyl acrylate, 90 g of isododecane and 1.2 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane are then introduced into the above mixture, still at 90°C and over 30 minutes.

The mixture is maintained at 90°C for 3 hours
15 and is then cooled.

A solution containing 50% polymer active material in isododecane is obtained.

A polymer comprising a poly(isobornyl methacrylate/isobutyl methacrylate) first block with a
20 Tg of 95°C, a polyisobutyl acrylate second block with a Tg of -20°C and an intermediate block which is an isobornyl methacrylate/isobutyl methacrylate/isobutyl acrylate random polymer is obtained.

This polymer has a weight-average mass of
25 100 700 and a number-average mass of 20 800, i.e. a polydispersity index I of 4.85.

Second embodiment

According to a second embodiment, the block polymer comprises a first block having a glass transition temperature (T_g) of between 20 and 40°C, in accordance with the blocks described in c) and a second block having a glass transition temperature of less than or equal to 20°C, as described above in b) or a glass transition temperature of greater than or equal to 40°C, as described in a) above.

10 Preferably, the proportion of the first block with a T_g of between 20 and 40°C ranges from 10% to 85%, better still from 30% to 80% and even better still from 50% to 70% by weight of the polymer.

When the second block is a block with a T_g of greater than or equal to 40°C, it is preferably present in a proportion ranging from 10% to 85%, better still from 20% to 70% and even better still from 30% to 70% by weight of the polymer.

When the second block is a block with a T_g of less than or equal to 20°C, it is preferably present in a proportion ranging from 10% to 85%, better still from 20% to 70% and even better still from 20% to 50% by weight of the polymer.

Preferably, the first block with a T_g of between 20 and 40°C is a copolymer derived from monomers which are such that the corresponding

homopolymer has a Tg of greater than or equal to 40°C, and from monomers which are such that the corresponding homopolymer has a Tg of less than or equal to 20°C.

Advantageously, the second block with a Tg of 5 less than or equal to 20°C or with a Tg of greater than or equal to 40°C is a homopolymer.

Thus, according to a first variant of this second embodiment, the block polymer may comprise:

- a first block with a Tg of between 20 and 40°C, for
10 example with a Tg of 25 to 39°C, which is a copolymer comprising at least one methyl acrylate monomer, at least one methyl methacrylate monomer and at least one acrylic acid monomer,
- a second block with a Tg of greater than or equal to
15 40°C, for example ranging from 85 to 125°C, which is a homopolymer composed of methyl methacrylate monomers, and
- an intermediate block comprising at least one methyl acrylate, methyl methacrylate monomer, and
- 20 - an intermediate block comprising methyl methacrylate, at least one acrylic acid monomer and at least one methyl acrylate monomer.

According to a second variant of this second embodiment, the block polymer may comprise:

- 25 - a first block with a Tg of between 20 and 40°C, for example with a Tg of 21 to 39°C, which is a copolymer

comprising isobornyl acrylate/isobutyl methacrylate/2-ethylhexyl acrylate,

- a second block with a Tg of less than or equal to 20°C, for example ranging from -65 to -35°C, which is a methyl methacrylate homopolymer, and
- an intermediate block which is an isobornyl acrylate/isobutyl methacrylate/2-ethylhexyl acrylate random copolymer.

According to a third variant of this second embodiment, the block polymer may comprise:

- a first block with a Tg of between 20 and 40°C, for example with a Tg from 21 to 39°C, which is an isobornyl acrylate/methyl acrylate/acrylic acid copolymer,
- a second block with a Tg of greater than or equal to 40°C, for example ranging from 85 to 115°C, which is an isobornyl acrylate homopolymer, and
- an intermediate block which is an isobornyl acrylate/methyl acrylate/acrylic acid random copolymer.

The composition of the invention advantageously contains from 0.1% to 60% by weight of active material (or solids), preferably from 0.5% to 50% by weight and more preferably from 1% to 40% by weight, of block polymer.

The composition according to the invention may comprise a hydrophilic medium comprising water or a

mixture of water and of hydrophilic organic solvent(s),
for instance alcohols and especially linear or branched
lower monoalcohols containing from 2 to 5 carbon atoms,
for instance ethanol, isopropanol or n-propanol, and
5 polyols, for instance glycerol, diglycerol, propylene
glycol, sorbitol, pentylene glycol and polyethylene
glycols, or alternatively hydrophilic C₂ ethers and C₂-
C₄ aldehydes.

The water or the mixture of water and of
10 hydrophilic organic solvents may be present in the
composition according to the invention in a content
ranging from 0.1% to 99% by weight and preferably from
10% to 80% by weight relative to the total weight of
the composition.

15 The composition according to the invention
comprises a cosmetically acceptable organic liquid
medium (acceptable tolerance, toxicology and feel).

According to one particularly preferred
embodiment, the organic liquid medium of the
20 composition contains at least one organic solvent,
which is the or one of the polymerization solvent(s)
for the block polymer as described above.
Advantageously, the said organic solvent is the liquid
that is in majority amount by weight in the organic
25 liquid medium of the cosmetic composition.

According to one embodiment, the organic

liquid medium comprises at least one fatty substance that is liquid at room temperature (in general 25°C). This liquid fatty substance may be of animal, plant, mineral or synthetic origin.

- 5 As fatty substances that are liquid at room temperature, often known as oils, which may be used in the invention, mention may be made of: hydrocarbon-based oils of animal origin such as perhydrosqualene; hydrocarbon-based plant oils such as liquid
- 10 triglycerides of fatty acids containing from 4 to 10 carbon atoms, for instance heptanoic or octanoic acid triglycerides, or alternatively sunflower oil, corn oil, soybean oil, grapeseed oil, sesame seed oil, apricot oil, macadamia oil, castor oil, avocado oil,
- 15 caprylic/capric acid triglycerides, jojoba oil or shea butter; linear or branched hydrocarbons, of mineral or synthetic origin, such as liquid paraffins and derivatives thereof, petroleum jelly, polydecenes, and hydrogenated polyisobutene such as parleam; synthetic
- 20 esters and ethers, especially of fatty acids, for instance purcellin oil, isopropyl myristate, 2-ethylhexyl palmitate, 2-octyldodecyl stearate, 2-octyldodecyl erucate or isostearyl isostearate; hydroxylated esters, for instance isostearyl lactate,
- 25 octyl hydroxystearate, octyldodecyl hydroxystearate, diisostearyl malate, triisocetyl citrate, and fatty

alkyl heptanoates, octanoates or decanoates; polyol esters, for instance propylene glycol dioctanoate, neopentyl glycol diheptanoate or diethylene glycol diisononanoate; and pentaerythritol esters; fatty
5 alcohols containing from 12 to 26 carbon atoms, for instance octyldodecanol, 2-butyloctanol, 2-hexyldecanol, 2-undecylpentadecanol or oleyl alcohol; partially hydrocarbon-based and/or partially silicone-based fluoro oils; silicone oils, for instance volatile
10 or non-volatile, linear or cyclic polymethylsiloxanes (PDMS), for instance cyclomethicones, dimethicones optionally comprising a phenyl group, for instance phenyl trimethicones, phenyltrimethylsiloxydiphenylsiloxanes, diphenylmethyl
15 dimethyl trisiloxanes, diphenyl dimethicones, phenyl dimethicones and polymethylphenylsiloxanes; mixtures thereof.

These oils may be present in a content ranging from 0.01% to 90% and better still from 0.1% to
20 85% by weight relative to the total weight of the composition.

The organic liquid medium of the composition according to the invention may also comprise one or more cosmetically acceptable organic solvents
25 (acceptable tolerance, toxicology and feel).

These solvents may generally be present in a

content ranging from 0.1% to 90%, preferably from 10% to 90% and better still from 30% to 90% by weight relative to the total weight of the composition.

As solvents that may be used in the composition of the invention, mention may be made, besides the hydrophilic organic solvents mentioned above, of ketones that are liquid at room temperature, such as methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, isophorone, cyclohexanone and acetone; propylene glycol ethers that are liquid at room temperature, such as propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate and dipropylene glycol mono-n-butyl ether; short-chain esters (containing from 3 to 8 carbon atoms in total), such as ethyl acetate, methyl acetate, propyl acetate, n-butyl acetate and isopentyl acetate; ethers that are liquid at room temperature, such as diethyl ether, dimethyl ether and dichlorodiethyl ether; alkanes that are liquid at room temperature, such as decane, heptane, dodecane, isododecane and cyclohexane; cyclic aromatic compounds that are liquid at room temperature, such as toluene and xylene; aldehydes that are liquid at room temperature, such as benzaldehyde and acetaldehyde, and mixtures thereof.

The composition may comprise, besides the block polymer described above, an additional polymer

such as a film-forming polymer. According to the present invention, the term "film-forming polymer" means a polymer that is capable of forming, by itself or in the presence of an auxiliary film-forming agent, 5 a continuous film that adheres to a support, especially to keratin materials.

Among the film-forming polymers that may be used in the composition of the present invention, mention may be made of synthetic polymers, of free- 10 radical type or of polycondensate type, polymers of natural origin, and mixtures thereof. Film-forming polymers that may be mentioned in particular include acrylic polymers, polyurethanes, polyesters, polyamides, polyureas and cellulose-based polymers, for 15 instance nitrocellulose.

The polymer may be combined with one or more auxiliary film-forming agents. Such a film-forming agent may be chosen from any compound known to those skilled in the art as being capable of fulfilling the 20 desired function, and may be chosen especially from plasticizers and coalescers.

The composition according to the invention may comprise at least one wax. For the purposes of the present invention, the term "wax" means a lipophilic 25 compound that is solid at room temperature (25°C), which undergoes a reversible solid/liquid change of

state, and which has a melting point of greater than or equal to 30°C, which may be up to 120°C.

The melting point of the wax may be measured using a differential scanning calorimeter (DSC), for
5 example the calorimeter sold under the name DSC 30 by the company Mettler.

The waxes may be hydrocarbon-based waxes, fluoro waxes and/or silicone waxes and may be of plant, mineral, animal and/or synthetic origin. In particular,
10 the waxes have a melting point of greater than 25°C and better still greater than 45°C.

As waxes that may be used in the composition of the invention, mention may be made of beeswax, carnauba wax or candelilla wax, paraffin, microcrystal-
15 line waxes, ceresin or ozokerite; synthetic waxes, for instance polyethylene waxes or Fischer-Tropsch waxes, and silicone waxes, for instance alkyl or alkoxy dimethicones containing from 16 to 45 carbon atoms.

The nature and amount of the solid fatty
20 substances depend on the desired mechanical properties and textures. As a guide, the composition may contain from 0% to 50% by weight and better still from 1% to 30% by weight of waxes, relative to the total weight of the composition.

25 The composition according to the invention may also comprise one or more dyestuffs chosen from

water-soluble dyes and pulverulent dyestuffs, for instance pigments, nacles and flakes that are well known to those skilled in the art. The dyestuffs may be present in the composition in a content ranging from
5 0.01% to 50% by weight and preferably from 0.01% to 30% by weight, relative to the weight of the composition.

The term "pigments" should be understood as meaning white or coloured, mineral or organic particles of any shape, which are insoluble in the physiological
10 medium and which are intended to colour the composition.

The term "nacles" should be understood as meaning iridescent particles of any shape, produced especially by certain molluscs in their shell, or
15 alternatively synthesized.

The pigments may be white or coloured, and mineral and/or organic. Among the mineral pigments that may be mentioned are titanium dioxide, optionally surface-treated, zirconium oxide or cerium oxide, and
20 also zinc oxide, iron oxide (black, yellow or red) or chromium oxide, manganese violet, ultramarine blue, chromium hydrate and ferric blue, and metal powders, for instance aluminium powder or copper powder.

Among the organic pigments that may be
25 mentioned are carbon black, pigments of D & C type, and lakes based on cochineal carmine or on barium,

strontium, calcium or aluminium.

Mention may also be made of pigments with an effect, such as particles comprising a natural or synthetic, organic or mineral substrate, for example
5 glass, acrylic resins, polyester, polyurethane, polyethylene terephthalate, ceramics or aluminas, the said substrate being uncoated or coated with metal substances, for instance aluminium, gold, silver, platinum, copper or bronze, or with metal oxides, for
10 instance titanium dioxide, iron oxide or chromium oxide, and mixtures thereof.

The nacreous pigments may be chosen from white nacreous pigments such as mica coated with titanium or with bismuth oxychloride, coloured nacreous
15 pigments such as titanium mica coated with iron oxides, titanium mica coated especially with ferric blue or chromium oxide, titanium mica coated with an organic pigment of the abovementioned type and also nacreous pigments based on bismuth oxychloride. Interference
20 pigments, especially liquid-crystal pigments or multilayer pigments, may also be used.

The water-soluble dyes are, for example, beetroot juice or methylene blue.

The composition according to the invention
25 may comprise one or more fillers, especially in a content ranging from 0.01% to 50% by weight and

preferably ranging from 0.01% to 30% by weight, relative to the total weight of the composition. The term "fillers" should be understood as meaning colourless or white, mineral or synthetic particles of any shape, which are insoluble in the medium of the composition, irrespective of the temperature at which the composition is manufactured. These fillers serve especially to modify the rheology or the texture of the composition.

10 The fillers may be mineral or organic in any form, platelet-shaped, spherical or oblong, irrespective of the crystallographic form (for example leaflet, cubic, hexagonal, orthorhombic, etc.). Mention may be made of talc, mica, silica, kaolin, polyamide
15 (Nylon®) powders (Orgasol® from Atochem), poly- β -alanine powder and polyethylene powder, powders of tetrafluoroethylene polymers (Teflon®), lauroyllysine, starch, boron nitride, hollow polymer microspheres such as those of polyvinylidene chloride/acrylonitrile, for
20 instance Exapancel® (Nobel Industrie) or acrylic acid copolymers (Polytrap® from the company Dow Corning) and silicone resin microbeads (for example Tospearls® from Toshiba), elastomeric polyorganosiloxane particles, precipitated calcium carbonate, magnesium carbonate,
25 magnesium hydrocarbonate, hydroxyapatite, hollow silica

microspheres (Silica Beads® from Maprecos), glass or ceramic microcapsules, and metal soaps derived from organic carboxylic acids containing from 8 to 22 carbon atoms and preferably from 12 to 18 carbon atoms, for example zinc, magnesium or lithium stearate, zinc laurate or magnesium myristate.

The composition according to the invention may especially be in the form of a suspension, a dispersion, a solution, a gel, an emulsion, especially an oil-in-water (O/W) emulsion, a water-in-oil (W/O) emulsion or a multiple emulsion (W/O/W or polyol/O/W or O/W/O emulsion), in the form of a cream, a paste, a mousse, a dispersion of vesicles, especially of ionic or nonionic lipids, a two-phase or multi-phase lotion, a spray, a powder, a paste, especially a soft paste (especially a paste with a dynamic viscosity at 25°C of about from 0.1 to 40 Pa.s under a shear rate of 200 s⁻¹, after measurement for 10 minutes in cone/plate geometry). The composition may be anhydrous; for example, it may be a soft anhydrous paste.

A person skilled in the art may select the appropriate galenical form, and also the method for preparing it, on the basis of his general knowledge, taking into account firstly the nature of the constituents used, especially their solubility in the support, and secondly the intended application for the

composition.

The composition according to the invention may be a makeup composition, for instance products for the complexion (foundations), makeup rouges,
5 eyeshadows, liquid lipsticks, concealer products, mascaras, eyeliners, eyebrow makeup products, nail products, such as nail varnishes, body makeup products or hair makeup products (hair mascara or hair lacquer).

The composition according to the invention
10 may also be a care product for body and facial skin, especially an antisen product or a skin-colouring product (such as a self-tanning product).

A subject of the present invention is also a cosmetic assembly comprising:

- 15 i) a container delimiting at least one compartment, the said container being closed by a closing member; and
ii) a composition as described above, placed inside the said compartment.

20 The container may be in any adequate form. It may especially be in the form of a bottle, a tube, a jar, a case, a box, a sachet or a carton.

The closing member may be in the form of a removable stopper, a lid, a cap, a tear-off strip or a
25 capsule, especially of the type comprising a body attached to the container and a cover cap articulated

on the body. It may also be in the form of a member for selectively closing the container, especially a pump, a valve or a flap valve.

The container may be combined with an
5 applicator, especially in the form of a brush comprising an arrangement of bristles maintained by a twisted wire. Such a twisted brush is described especially in patent US 4 887 622. It may also be in the form of a comb comprising a plurality of
10 application members, obtained especially by moulding. Such combs are described, for example, in patent FR 2 796 529. The applicator may be in the form of a fine brush, as described, for example, in patent FR 2 722 380. The applicator may be in the form of a
15 block of foam or of elastomer, a felt or a spatula. The applicator may be free (tuft or sponge) or securely fastened to a rod borne by the closing member, as described, for example, in patent US 5 492 426. The applicator may be securely fastened to the container,
20 as described, for example, in patent FR 2 761 959.

The product may be contained directly in the container, or indirectly. By way of example, the product may be arranged on an impregnated support, especially in the form of a wipe or a pad, and arranged
25 (individually or in plurality) in a box or in a sachet. Such a support incorporating the product is described,

for example, in patent application WO 01/03538.

The closing member may be coupled to the container by screwing. Alternatively, the coupling between the closing member and the container is done
5 other than by screwing, especially via a bayonet mechanism, by click-fastening, gripping, welding, bonding or by magnetic attraction. The term "click-fastening" in particular means any system involving the crossing of a bead or cord of material by elastic
10 deformation of a portion, especially of the closing member, followed by return to the elastically unconstrained position of the said portion after the crossing of the bead or cord.

The container may be at least partially made
15 of thermoplastic material. Examples of thermoplastic materials that may be mentioned include polypropylene or polyethylene.

Alternatively, the container is made of non-thermoplastic material, especially glass or metal (or
20 alloy).

The container may have rigid walls or deformable walls, especially in the form of a tube or a tubular bottle.

The container may comprise means for
25 distributing or facilitating the distribution of the composition. By way of example, the container may have

deformable walls so as to allow the composition to exit
in response to a positive pressure inside the
container, this positive pressure being caused by
elastic (or non-elastic) squeezing of the walls of the
5 container.

The container may consist of a carton with a
base delimiting at least one housing containing the
composition, and a lid, especially articulated on the
base, and capable of at least partially covering the
10 said base. Such a carton is described, for example, in
patent application WO 03/018423 or in patent
FR 2 791 042.

The container may be equipped with a drainer
arranged in the region of the aperture of the
15 container. Such a drainer makes it possible to wipe the
applicator and possibly the rod to which it may be
securely fastened. Such a drainer is described, for
example, in patent FR 2 792 618.

The composition may be at atmospheric
20 pressure inside the container (at room temperature) or
pressurized, especially by means of a propellant gas
(aerosol). In the latter case, the container is
equipped with a valve (of the type used for aerosols).

The content of the patents or patent
25 applications mentioned above are incorporated by
reference into the present patent application.

The examples that follow illustrate the compositions according to the invention in a non-limiting manner.

Examples 8 to 12: Lipsticks

5

| Example | 8 | 9 | 10 | 11 | 12 |
|---|------|------|------|------|------|
| Polymer of Example 2 | 90.7 | | | | |
| Polymer of Example 3 | | 90.7 | | | |
| Polymer of Example 4 | | | 90.7 | | |
| Polymer of Example 6 | | | | 90.7 | |
| Polymer of Example 7 | | | | | 90.7 |
| Hydrogenated polyisobutene | 2.1 | 2.1 | 2.1 | 2.1 | 2.1 |
| Octyldodecanol | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 |
| Phenyl trimethicone (DC 556, 20 cSt, Dow Corning) | 2.1 | 2.1 | 2.1 | 2.1 | 2.1 |
| Copolymer vinylpyrrolidone/ 1-eicosene (Antaron V-220, ISP) | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 |
| Pigments | 3 | 3 | 3 | 3 | 3 |

Procedure

1. A ground pigmentary mixture of the pigments in the oily phase is prepared by treating the mixture three
10 times in a three-roll mill.
2. The ground material required for the composition and the other ingredients are weighed out in a beaker.

3. The mixture is stirred using a Rayneri blender for 45 minutes at room temperature.

4. The formula is cast in isododecane-leaktight cooling boxes.

5

Gloss measurement

1. Films with a wet thickness of 50 and/or 150 μm are prepared using a mechanical applicator. The depositions are made on a Leneta brand contrast card with reference Form 1A Penopac.
2. The films are left to dry for 24 hours at a regulated temperature of 30°C.
3. The gloss measurements are performed using a Byk Gardner micro-tri-gloss glossmeter with measuring angles of 20° and 60° for each series of deposits.

The gloss results obtained in vivo are given in the table below:

150 μm deposit

| Angle | Deposit | Polymer | Mean (%) | Standard deviation |
|--------------|---------------------------|-----------|----------|--------------------|
| Angle of 20° | 150 μm deposit | Example 8 | 54.2 | 2.0 |
| | | Example 9 | 41.0 | 3.5 |
| Angle of 60° | 150 μm deposit | Example 8 | 75.7 | 0.8 |

| | | | | |
|--|--|-----------|------|-----|
| | | Example 9 | 73.6 | 1.6 |
|--|--|-----------|------|-----|

50 μm deposit

| Angle | Deposit | Polymer | Mean (%) | Standard deviation |
|-----------------|-----------------------------|-----------|----------|--------------------|
| Angle of 20° | 50 μm deposit | Example 8 | 47.6 | 1.2 |
| | | Example 9 | 42.6 | 5.2 |
| Angle of 60° | 50 μm deposit | Example 8 | 69.3 | 0.7 |
| | | Example 9 | 74.8 | 1.0 |

5 The mean gloss obtained is greater than 40 out of 100 for a measuring angle of 20° and a thickness of 50 μm or 150 μm .

 The mean gloss obtained is greater than 65 out of 100 for a measuring angle of 60° and a thickness
10 of 50 μm . The mean gloss obtained is greater than 70 out of 100 for a measuring angle of 60° and a thickness of 150 μm .

Example 13: Nail varnish

| | |
|----------------------|-----------|
| Polymer of Example 1 | 23.8 g AM |
| Butyl acetate | 24.99 g |
| Isopropanol | 10.71 g |

| | |
|--|-------|
| Hexylene glycol | 2.5 g |
| DC Red 7 Lake | 1 g |
| Hectorite modified with distearyl- dimethylbenzylammonium chloride (Bentone [®] 27V from Elementis) | 1.3 g |

Example 14: Nail varnish

| | |
|--|-----------|
| Polymer of Example 5 | 23.8 g AM |
| Butyl acetate | 24.99 g |
| Isopropanol | 10.71 g |
| Hexylene glycol | 2.5 g |
| DC Red 7 Lake | 1 g |
| Hectorite modified with distearyl- dimethylbenzylammonium chloride (Bentone [®] 27V from Elementis) | 1.3 g |
| Ethyl acetate | qs 100 g |